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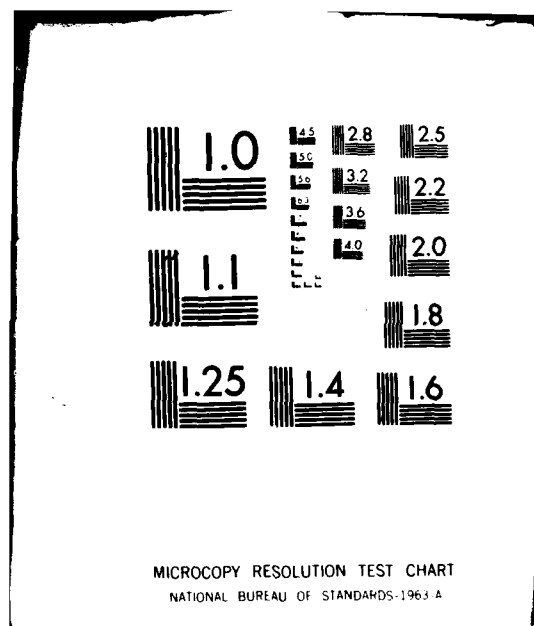
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INVERSION OF SPECTRAL LINESHAPES TO YIELD COLLISIONAL RATE CONS--ETC (11)
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② INVERSION OF SPECTRAL LINESHAPES TO YIELD COLLISIONAL RATE CONSTANTS.

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) State-to-state collisional energy transfer rates are being obtained by the inversion of pressure broadened linewidth data. Measurements of linewidths in overtone vibration-rotation transitions have yielded information rotationally elastic and inelastic collision rates for vibrationally excited HCl. Work is continuing in acquiring similar information for vibrationally excited HF and DF using tunable laser photoacoustic spectroscopy.		

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I. Background and Summary

Collisional energy transfer rates are of central importance to a large number of practical phenomena and devices. Much is known about collisional transitions for molecules in low levels of excitation. Because of the extreme experimental difficulty with conventional double resonance or laser fluorescence techniques little is known about how the mechanism of energy transfer changes with vibrational excitation. However, it is just these rates for highly vibrationally excited molecules that are important in practical situations of concern to the Navy. This is particularly true in high temperature environments such as combusting gases and the high levels of excitation that are found in laser devices and the interaction of laser energy with matter. We have been successful in obtaining rotational collisional transfer rates for highly vibrationally excited molecules by the inversion of pressure broadened linewidths in overtone vibration-rotation spectra. We will continue this important research employing a sensitive laser photoacoustic spectrometer, which was constructed during the initial phase of this contract, to measure these weak overtone absorptions. We also plan to extend this joint theoretical and experimental approach to other areas of spectroscopy which, with the appropriate theoretical treatment, will yield other new and interesting dynamical information.

The determination of any individual collisional transition rate from a single bulk experiment, such as pressure broadening, has been considered difficult in the past because the pressure broadened linewidth is not very sensitive to any one component rate. In our approach to the inversion of linewidths to yield state-to-state rates we are utilizing recently developed scaling relationships which fix the ratios of many rates within a family to a fundamental rate in that class, e.g., rotation-rotation or rotation-translation collisions. The small

number of fundamental rates can then be determined by a small number of independent linewidth measurements. Also determined are dynamical factors which allow one to calculate the elastic contributions such as dephasing, and the change in the various contributions to the linewidth with the vibrational excitation of the collision partners.

There are two specific advantages to acquiring state-to-state rates by this type of procedure. First, molecular beam or laser fluorescence experiments usually required for state-to-state measurements are very complex. Because of the requirements of the detection or pumping techniques employed in these procedures, they are amenable only to a limited number of atoms or molecules. Spectroscopic measurements can be done on practically any species. Second, and most important, experiments that employ state-to-state pumping and subsequent detection of relaxation require that an appreciable fraction of molecules be excited into the specific state from which relaxation is being followed. However, transitions from the ground vibrational state to highly vibrationally excited states are extraordinarily weak, making it impossible to observe relaxation from these states if a substantial number of molecules must be initially populated. One can acquire simple absorption spectra for transitions to much higher states than would be feasible for other techniques because the ability to measure an absorption line does not depend on the absolute number of molecules promoted to the upper state but rather on the fraction of light absorbed.

Though they are of immediate importance, we do not consider the simple acquisition of rate data for certain molecules to be the only purpose of our research. It is important to obtain specific rates for many different molecules and collision partners and tie these together to obtain an understanding of the observed trends in terms of the fundamental aspects of the collision dynamics. Of course this more basic understanding is of much greater practical importance

than the individual rates alone because it will allow us to correlate and predict the behavior of important chemical systems and many useful devices.

II. Progress Report

The specific approach taken during the initial period of this contract has been four-fold.

1. We have acquired overtone band absorption data outside our own laboratory with a conventional Fourier transform spectrometer and a long path length White cell.
2. These data were used to stimulate the development of the necessary inversion procedures for the molecule-molecule case.
3. While the necessary theoretical developments were taking place we have constructed the laser photoacoustic system which will be required for carrying out the laboratory measurements needed on HF and DF.
4. We have begun utilizing a Fourier transform spectrometer at Western Electric Corporation in Princeton, New Jersey, to acquire the fundamental and first overtone bands of the hydrogen halides.

Our first data on the overtone bands of HCl which were taken at Kitt Peak National Observatory have been completely reduced.¹ These data have been successfully inverted to yield the rotation-rotation, rotation-translation and dephasing contributions to the line widths.² The inversion of the HCl overtone linewidths required a more sophisticated application and implementation of the scaling theory than had been done for the atom-molecule case.³ Previously only the scaling of rotation-translation inelastic rates was considered. In the molecule-molecule case for overtone absorptions, the mechanisms contributing to the linewidth are much more complex requiring the additional consideration of rotation-rotation rates, elastic dephasing effects, and their changes with vibrational excitation. Having the accurate HCl data over a wide range of overtone bands stimulated the development of the necessary procedures and served as a check of their efficacy.

Some of the rotation-rotation rate constants that were obtained in this manner are shown in Figure 1. These rates are for collisions in which both collision partners are in the ground vibrational state and for which one molecule loses one quanta of rotational energy and the other molecule gains one quanta. Two curves are shown. One curve is for molecule number one in state $j = 3$ and the other is for molecule number one in state $j = 8$. Note the strong enhancement of the rate for the resonant up-down collision in which molecule number two is in state $j_2 = j_1 - 1$. An important feature of these results, however, is that the off resonant rates do not diminish rapidly as the difference between the j state of the collision partners increases. One can obtain the rotational relaxation rates for vibrationally excited collision partners by utilizing the appropriate dynamical factors which are also obtained as part of the inversion procedure. Thus we have shown that it is possible to obtain a stable inversion of overtone pressure broadening data to yield an enormous amount of important dynamical information about collisions of vibrationally excited molecules.

This research is being continued using a laser photoacoustic system to study the overtone bands of HF and DF. We plan to check the accuracy of this apparatus by first doing some measurements on HCl and comparing them to the Kitt Peak data. All of the component subsystems of the laser photoacoustic setup have been constructed and tested. The system presently comprises a krypton-ion laser pumped dye laser system with an intracavity photoacoustic cell. The laser output is modulated with a mechanical chopper wheel. The output of the photoacoustic cell is synchronously detected with a lock-in amplifier and the data is first digitized and then transferred to the memory of an AIM 65 microcomputer. The AIM 65 microcomputer also digitizes the output fringes of a wavelength monitoring Fabry-Perot etalon, and the output of a photodiode which monitors the intensity of the dye laser. Data which is stored in the microcomputer can be transferred by a

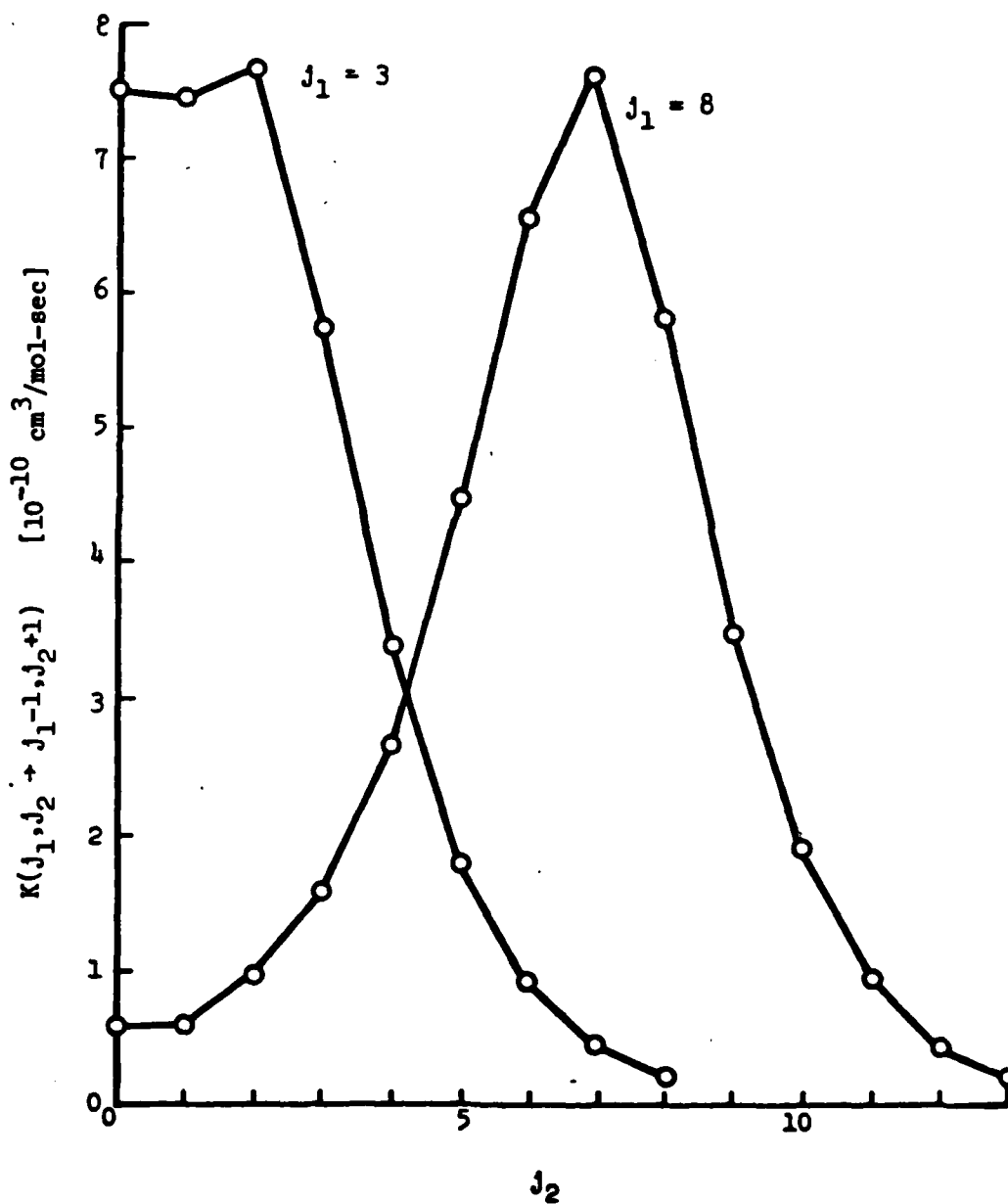


Figure 1 - Typical rotation-rotation transfer rates for HCl-HCl collisions obtained by the inversion of pressure broadening data.

telephone link to an IBM 3033 computer where the spectra can be reduced and fitted with a nonlinear least squares fitting routine which we have developed for this purpose.⁴

A majority of the pressure broadening data in the literature on the pure rotational, fundamental, and first-overtone bands of the molecules of interest to us were taken before the development of modern high resolution infrared spectrometers. Consequently, this data typically has an accuracy of only 10 to 15%.⁵ It will be necessary for us to re-acquire these spectra and obtain the necessary pressure broadening information to a much higher accuracy in order to obtain complete information about the changes in collision dynamics with increasing vibrational excitation. We are presently concentrating on obtaining the fundamental and first overtone band pressure broadening data on the hydrogen halides using the Fourier transform infrared spectrometer at Western Electric Corporation in Princeton, New Jersey. We are at this time completing the construction of a corrosion resistant vacuum system and appropriate absorption cell which has been designed to fit the Western Electric spectrometer. We are also in the process of testing the data transfer setup that will be used to transfer the spectra to our own computer center. Self-broadening in HF, DF and HCl will be done in the immediate future. Other molecules and collision partners will be done as we acquire their overtone spectra with the laser photoacoustic spectrometer.

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III. Publications During the Term of This Contract

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2. M. Zughul, J. Gelfand, H. Rabitz and A. DePristo, "Pressure Broadening in the 0-4 through 0-7 Overtone Bands of H³⁵Cl and H³⁷Cl", JQSRT, submitted (1980).
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6. A. DePristo, J. Gelfand and H. Rabitz, "State-to-State Rates of Vibrationally Excited HCl by Inversion of Overtone Band Pressure Broadening Measurements", Chem. Phys. Letts., in preparation (1980).

IV. Graduate Students and Postdoctoral Personnel Associated with this Contract

Ms. Elizabeth Wilczek, Masters Degree Candidate.

Dr. Joseph BelBruno, Postdoctoral Research Associate.

V. CURRENT SUPPORT

	Supporting Agency	Project Title	Dates	Award Amount	Man-Months or % of Effort Committed
I. Gelfand, Miles, Rabitz Joint Contracts					
A. Current Support	NSF	Experimental and Theoretical Study of Relaxation from Highly Vibrationally Excited Hydrogenic Molecules	8-1-78 36 mo.	\$219,000	Gelfand 18 mo. Miles 3 mo. Rabitz 3 mo. (summer)
	ONR	Inversion of Spectral Line Shapes to Yield Collisional Rate Constants	9-1-78 24 mo.	113,125	Gelfand 7 mo.
	Exxon	Development of Laser Applications	9-1-78 12 mo.	10,000	
II. Gelfand, Miles, Royce Joint Contracts					
A. Current Support	NSF	Laser Source for Materials Research	8-1-79 12 mo.	23,000	
III. H. Rabitz					
A. Current Support	ONR	Collisional Studies of Gaseous Molecular Lasers	4-1-80 12 mo.	75,000	1/2 summer
	DOE	Inelastic Molecular Collisions: Applicability of Theoretical Methods to Problems in Relaxation Phenomena and Laser Operation	2-1-80	62,000	
(with A. Askar, A. Cakmak)	NSF	Finite Element Method for Atom-Molecule Reactive Scattering	11-1-79 36 mo.	93,400	1/2 summer
(with S. Augustin)	AFOSR	Non-Equilibrium Statistical Mechanics	9-30-79 12 mo.	52,070	
	ONR	Kinetic Studies of Combustion Systems	3-15-80 12 mo.	23,443	

Supporting Agency	Project Title	Dates	Award Amount	Man-Months or % of Effort Committee
IV. <u>R.B. Miles</u>				
NSF	Coherent Anti-Stokes Raman Scattering from Surfaces	9-1-78 24 mo.	92,512	summer
NASA/Ames	Turbulence Measurements in High Speed Flows by Resonance Fluorescence	1-1-79 24 mo.	89,239	1 mo. academic year

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